Thermodynamic similarity of stacked-cup multiwall carbon nanotubes and graphite

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This work presents the results of the investigation of physico-chemical properties for stacked-cup multiwall carbon nanotubes (MCNT) supplied by Vision Development (Japan) and synthesized by the gas-phase catalytic pyrolysis of hydrocarbons according to the method [1]. It was shown in [2] that the apparent density of MCNT (2210 ± 22) kg·m^{-3} at T = 293 K determined in water, toluene, and [C$_4$mim]PF$_6$ and the distance between the layers of 0.36 nm are close to the corresponding values for hexagonal graphite being 2260 kg·m^{-3} and 0.3635 nm, respectively.

The heat capacities of MCNT samples in the temperature range of (5 to 370) K have been measured and their energies of combustion have been determined. The thermodynamic parameters of pure (without incapsulated Ni) MCNT were evaluated. The average energy of combustion for pure MCNT is close to the corresponding value for graphite (Table). The difference between their energies of combustion is only ~170 J·g^{-1}. Thus, we can conclude that MCNT and graphite are similar not only geometrically, but also thermodynamically. From the Table, it also follows that graphite and MCNT are much more thermochemically stable (about 3 kJ·g^{-1}) forms of carbon compared to fullerenes C$_{60}$ and C$_{70}$.

The energy of combustion for some carbon materials at T = 298.15 K

Compound	Graphite	MCNT*	C$_{60}$	C$_{70}$
$-\Delta_c U^o_{298}$, J·g^{-1}	32764 ± 4 [3]	32595 ± 13	36017 ± 17 [4]	35802 ± 26 [4]

* for pure (without Ni content) sample

It was found that the heat capacities of MCNT, graphite and fullerenes C$_{60}$ and C$_{70}$ per one mole of carbon atoms are consistent within ±3 % in the temperature interval of (300 to 350) K. Taking into account this fact the extrapolation of the heat capacity of MCNT was carried out up to T = 2000 K and thermodynamic properties of nanotubes in the temperature range of (0 to 2000) K were calculated.

Thermodynamic analysis of reactions for the synthesis of graphite and MCNT by pyrolysis of carbon-containing gases (CO, CO$_2$, CH$_4$, C$_3$H$_8$, C$_4$H$_{10}$) was performed. The following results were obtained.

1. Hydrogen H$_2$ (~ 82 mol·kg^{-1}) and solid graphite and MCNT (~ 65 mol·kg^{-1}) are the main components of the equilibrium mixtures obtained by the pyrolysis of hydrocarbons C$_n$H$_{2n+2}$ at T ≥ 1300 K (P = 1 bar).

2. The equilibrium of the reaction $2CO_{(gas)} \leftrightarrows CO_{2(gas)} + C_{(graphite)}$ ($C_{(MCNT)}$) is almost completely shifted to the right side of the equation in the range of (298 to 900) K.

3. The synthesis of fullerenes C$_{60}$ and C$_{70}$ from graphite is thermodynamically possible only through the high temperature (T > 3000 K) sublimation of carbon.

References

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